

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number:

0 404 727
A2

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 90810440.9

(5) Int. Cl.⁵ **C08L 3/02, C08L 57/10,**
C08L 33/00

(22) Date of filing: 18.06.90

D
#6

(30) Priority: 22.06.89 US 369978
02.11.89 US 430764

(43) Date of publication of application:
27.12.90 Bulletin 90/52

(54) Designated Contracting States:
AT BE CH DE DK ES FR GB GR IT LI LU NL SE

(71) Applicant: WARNER-LAMBERT COMPANY
201 Tabor Road
Morris Plains New Jersey 07950(US)

(72) Inventor: Lentz, David John, Dr.
23 Timber Lane
Randolph, N.J. 07869(US)
Inventor: Sachetto, Jean-Pierre, Dr.
Düchelweiher 13
CH-4144 Arlesheim(CH)
Inventor: Silbiger, Jakob, Dr.
Oberwilerstrasse 72
CH-4054 Basel(CH)

(74) Representative: Silbiger, Jakob, Dr.
c/o CAPSUGEL AG Fabrikmattenweg 2-4
CH-4144 Arlesheim(CH)

(54) Polymer base blend compositions containing destructureized starch.

(57) A thermoplastic polymer composition comprising

a) a destructureized starch, and

b) at least one polymer which does not contain hydroxyl groups and is selected from the group consisting of polymers which contain at least two types of functional groups bound to the same molecule one type of these groups being carboxylate groups; said polymer being present in an amount effective to enhance the physical properties of said articles.

The composition may contain further conventional additives as well as hydrophobic, substantially water-insoluble polymers.

EP 0 404 727 A2

no comp

Polymer base blend compositions containing destructurized starch

The present invention relates to polymer compositions capable of being formed by heat and pressure into articles having dimensional stability and enhanced physical properties, and to pre-mixes useful for preparing these compositions. These compositions and pre-mixes comprise destructurized starch and other polymers as described herein.

5 It is known that natural starch which is found in vegetable products and which contains a defined amount of water can be treated at an elevated temperature and in a closed volume, thereby at elevated pressures, to form a melt. The process is conveniently carried out in an injection molding machine or extruder. The starch is fed through the hopper onto a rotating, reciprocating screw. The feed material moves along the screw towards the tip. During this process, its temperature is increased by means of
10 external heaters around the outside of the barrel and by the shearing action of the screw. Starting in the feed zone and continuing in the compression zone, the particulate feed becomes gradually molten. It is then conveyed through the metering zone, where homogenization of the melt occurs, to the end of the screw. The molten material at the tip can then be treated further by injection molding or extrusion or any other known technique to treat thermoplastic melts, to obtain shaped articles.

15 This treatment, which is described in the European Patent Application No. 84 300 940.8 (Publication No. 118 240) which patent is incorporated herein by reference, yields an essentially destructurized starch. As described in the above mentioned patent, the reason for this is that the starch is heated above the glass transition and the melting temperatures of its components. As a consequence, a melting and disordering of the molecular structure of the starch granules takes place, so that an essentially destructurized starch is
20 obtained. The expression "destructurized starch" defines starch obtained by such thermoplastic melt formation. Reference is also made to European Patent Applications No. 88810455.1 (Publication No. 298,920), No. 88810548.3 (Publication No. 304,401) and No. 89810046.6 (Publication No. 326,517) which further describe destructurized starch, methods for making it, and uses of it. These application are also incorporated herein by reference.

25 It is preferred that the destructurized starch used in the present invention has been heated to a high enough temperature and for a time long enough so that the specific endothermic transition analysis as represented by differential scanning calorimetry (DSC) indicates that a specific relatively narrow peak just prior to oxidative and thermal degradation has disappeared, as described in the above-mentioned European Patent Application No. 89810046.6 (Publication No. 326 517).

30 Destructurized starch is a new and useful material for many applications. An important property is its biodegradability. In humid air, however, destructurized starch takes up water from the air, thereby increasing its moisture content. As a consequence, a shaped article made from destructurized starch may under such conditions lose its dimensional stability. On the other hand such an article may dry out in low humidity and become brittle.

35 Thermoplastic starch has unique properties and while these are very useful, they may limit its utility in cases where a softer, more resilient or harder, tougher polymer is desired.

Thermoplastic starch as mentioned can be extruded and molded into numerous useful shapes and profiles. However, the processing parameters such as water content, temperature, and pressure are generally critical and must be narrowly controlled to achieve reproducible quality products. This is a further
40 disadvantage for many applications.

To overcome these potential limitations, it would be useful to increase the dimensional stability over a wide humidity range; to increase the toughness (measured as break energy); to increase the elasticity (measured as elongation); to decrease polymer stiffness (measured as Young's modulus) and increase the hardness.

45 Broadening processing latitude increases the variety of shapes and composites and decreases the need for close controls. It would therefore also be useful to improve the control of the melt strength, e.g. increasing the processing latitude for extruding, injection molding, film blowing or fiber drawing and to control the surface tack and adhesion to other substrates.

Conventional thermoplastic materials are hydrophobic, substantially water-insoluble polymers which are
50 conventionally processed in the absence of water and volatile materials. Starch to the contrary forms a melt in the presence of water but decomposes at elevated temperature, i.e. around 240°C. It was therefore expected that such a starch melt could not be used as a thermoplastic component together with hydrophobic, substantially water-insoluble polymeric materials not only because starch forms a melt in the presence of water as described above, but also because of its chemical structure and hydrophilic nature.

It has now been found that starch, when heated in a closed volume at proper moisture and temperature

conditions, as described above, to form a melt of destructured starch, is substantially compatible in its processing with melts formed by hydrophobic substantially water insoluble thermoplastic polymers and that the two types of molten materials show an interesting combination of properties, especially after the melt has solidified.

5 One very important aspect is the surprisingly improved dimensional stability of such destructured starch blended with such hydrophobic thermoplastic materials. Such polymer compositions are described in copending European Patent Application No. 89810078.9 (Publication No. 327,505) which is incorporated herein by reference. Although articles made from such compositions possess better dimensional stability than those made from destructured starch alone, the physical properties of the therein-described
10 compositions are not as good as might be desired for some end uses. In particular, it is important that articles made from destructured starch compositions retain sufficient strength and dimensional stability to perform their desired function while still being biodegradable after disposal.

It has now been found that articles made from such destructured starch blended with specific hydrophobic thermoplastic materials as described herein show a surprising increase in all or a part of their
15 physical properties and behaviour of their melts as to overcome the limitations as explained above. Moreover it was surprisingly found that many of the blends described herein show a significantly improved dimensional stability in humid air compared with non-blended destructured starch whilst retaining a surprisingly high degree of disintegration in contact with moisture water which in consequence leads to a high degree of biodegradability.

20 In order to achieve such properties, it has been found useful to make polymer compositions comprising:
a) destructured starch, b) at least one polymer which does not contain hydroxyl groups and is selected from the group consisting of polymers which contain at least two types of functional groups bound to the same molecule one type of these groups being carboxylate groups (referred to herein as "component b")), and optionally c) an substantially water-insoluble polymer different from those defined as component b). In
25 one aspect, the present invention relates to a composition comprising destructured starch and component b). This composition is useful itself for making finished articles, but it is primarily useful as a "pre-mix" for combining with the substantially water-insoluble polymer. In a second aspect, the invention comprises the ternary composition of destructured starch, component b), and at least one substantially water-insoluble polymer (component c)). These compositions may be in the form of powdery mixtures of the components,
30 melts, or solid forms. The invention also includes methods for making and using both above-described compositions and shaped articles made therefrom.

The compositions of the first aspect of the invention comprise:

a) destructured starch, and
b) at least one polymer which does not contain hydroxyl groups and is selected from the group
35 consisting of polymers which contain at least two types of functional groups bound to the same molecule one type of these groups being carboxylate groups.

Such polymer composition may optionally contain further additives.

Specifically, the first aspect of the present invention is a polymer composition capable of being formed into articles having substantial dimensional stability comprising:

40 a) destructured starch, and
b) at least one polymer which does not contain hydroxyl groups and is selected from the group consisting of polymers which contain at least two types of functional groups bound to the same molecule one type of these groups being carboxylate groups: said polymer being present in an amount effective to enhance the physical properties of said articles (which amount is sometimes referred to herein as an
45 "effective amount" of component b).

Preferably this polymer composition additionally comprises at least one component c):

c) a substantially water-insoluble thermoplastic polymer which does not fall within the definition of those compounds defined herein as component b).

The present invention includes said polymer compositions in the form of powdery mixtures of their
50 components, in the form of melts, or in solidified form.

Component b) is chosen as described herein to be substantially compatible with the starch and also to promote the compatibility of component c) with the combination of starch and component b).

The present invention further refers to a method of producing said polymer compositions in the molten or solid form as well as a method of producing shaped articles from said polymer compositions, and to the
55 resulting shaped articles made therefrom.

The polymer compositions of the present invention are prepared by admixing destructured starch, component b), and optionally component c), and any further additives. This mixture is then heated in a closed volume to elevated temperatures until a homogeneous melt is obtained, and shaped articles can be

formed therefrom.

An alternate method of producing the polymer compositions of the present invention comprises: Heating starch, which is in a condition to be destructurized, in a closed volume to elevated temperatures and at elevated pressures for a time sufficient to destructurize the starch and form a melt; adding component b) as well as other polymers and/or additives before, during or after such starch destructurization; and continuing to heat the mixture until a homogenous melt is obtained. It is preferred that component b) and, if desired, component c), as well as other additives be combined with the starch and the combination formed into a melt. The starch in this combination may be already wholly or partially destructurized or the destructurization may take place during melt formation.

The present invention further refers to the process of working said polymer composition under controlled water content, temperature and pressure conditions as a thermoplastic melt wherein said working process is any known process, such as, for example injection molding, blow molding, extrusion, coextrusion, compression molding, vacuum forming, thermoforming or foaming. All of these processes are collectively referred to herein as "forming".

The term "functional group" as used herein includes all known polar groups that may be bound to the polymer chain such as, for example, hydroxy, alkoxy, carboxy, carboxyalkyl, alkyl carboxy, halo, pyrrolidone, acetal, and the like. These groups should be selected from those which will not degrade the starch.

The term "carboxylate" as used herein includes groups of the formula

$-COO^-Me^+$

wherein Me^+ signifies NH_4^+ , or a mono- or polyvalent metallic cation, preferably an alkali or earth alkali cation or zinc, preferably sodium, magnesium or zinc.

The term "starch" as used herein includes chemically substantially non-modified starches as for example carbohydrates of natural, vegetable origin, composed mainly of amylose and/or amylopectin. They can be extracted from various plants, examples being potatoes, rice, tapioca, corn (maize), pea, and cereals such as rye, oats and wheat. Preferred is starch made from potatoes, corn, wheat or rice. Mixtures of starch obtained from these sources are contemplated. It further includes physically modified starches such as gelatinized or cooked starches, starches with a modified acid value (pH), e.g. where acid has been added to lower their acid value to a range of about 3 to about 6. Further included are starches, e.g. potato starch, in which the divalent ions like Ca^{+2} or Mg^{+2} -ions associated with the phosphate groups have been partially or completely washed out from the starch or optionally wherein the ions present in the starch have been replaced partially or wholly by the same or different mono- or polyvalent ions. It further includes pre-extruded starches, as described in the above-referenced European Patent Application No. 88810548.3 (Publication No. 304,401).

As described above, it has been found that starches, e.g. with a water content within the range of about 5 to about 40% by weight based on the weight of the composition, undergo a specific narrow endothermic transition on heating to elevated temperatures and in a closed volume just prior to the endotherm change characteristic of oxidative and thermal degradation. The specific endothermic transition can be determined by differential scanning calorimetric analysis (DSC) and is indicated on the DSC-diagram by a specific relatively narrow peak just prior to the endotherm characteristic of oxidative and thermal degradation. The peak disappears as soon as the mentioned specific endothermic transition has been undergone. The term "starch" includes also treated starches wherein said specific endothermic transition has been undergone. Such starch is described in the EP 89810046.6 (Publication No. 326,517).

Although at the current time, destructurization of starch requires the presence of water in ranges disclosed herein, the present inventive compositions also contemplate the use of destructurized starch prepared by other methods, e.g. without the use of water.

The water content of such a starch/water composition is preferably about 5 to about 40 % water by weight of the starch/water component and preferably about 5 to about 30 %. However, in order to work with the material near its equilibrium water content to which it gets when it is finally exposed to the free atmosphere, a water content of about 10 to about 22 %, preferably of about 14 to about 18 % by weight calculated based on the starch/water component should be used in processing and is preferred.

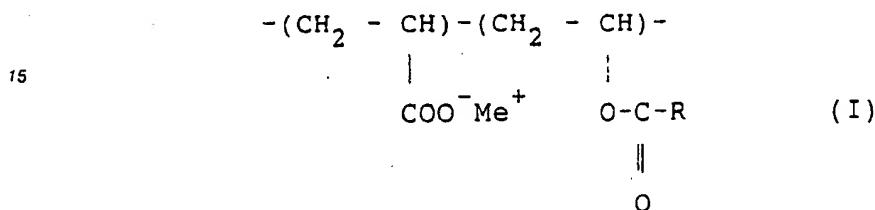
The polymer of the component b) is preferably a synthetic polymer, preferably a copolymer containing carboxylate groups as well as other units as are obtained by copolymerization of acrylic acid, methacrylic acid, crotonic acid, maleic acid, itaconic acid, e.g. in their acid or carboxylate form, with monomers such as ethylene, vinyl chloride, vinyl esters such as vinyl acetate, vinyl ethers, acrylic acid esters, acrylonitrile, methacrylic acid esters, maleic acid esters, acryl amide, omega-octadecene, vinyl-butyl ether, vinyl pyrrolidone and other known monomers. Such copolymers and their derivatives are known.

If a carboxyl group containing monomer is used for preparing the polymer, then at least a part of the

carboxyl groups must be neutralized with a cation as defined above. Such copolymers as well as methods for their production are known. Preferably the component b) substantially does not contain free acid groups.

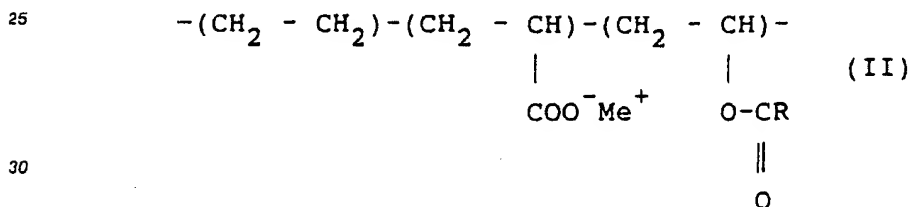
The polymers of component b) may have a general formula wherein the number of repeating units varies for each individual type of copolymer and is known per se as e.g. described in "Encyclopaedia of Polymer Science and Technology, Interscience Publ. Vol. 14, 1971". These copolymers may be exemplified by the following general formulas incorporating the mer units described above. The units within the brackets represent the individual mer units within each copolymer. These units may be combined in any known fashion, including random or block copolymerization. The molecular weight of the copolymer may be within known ranges.

10

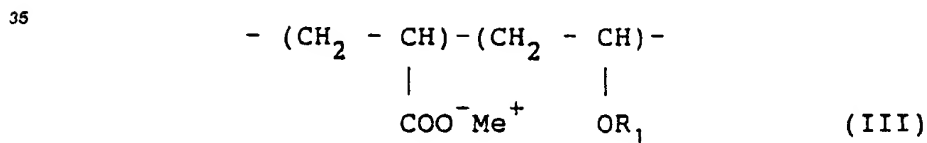


20

R is a saturated or unsaturated C₁ - C₂₁-hydrocarbon, preferably methyl, ethyl, propyl or butyl;



30



40

R₁ is alkyl (C₁ - C₄), preferably methyl.

Preferred copolymers of the component b) containing carboxylate groups are those which can be described as being derived from acrylic acid, methacrylic acid, crotonic acid, maleic acid, itaconic acid, methylacrylate, methylmethacrylate, acrylamide, acrylonitrile and/or methylvinylether.

More preferred polymers of the compound b) are those which can be described as being derived from acrylic acid, methacrylic acid, maleic acid, methacrylate, ethyl acrylate and/or methylvinylether. Such copolymers may be also copolymerized with ethylene, propylene, or styrene, which within the scope of this invention are not considered as a "functional group".

Such preferred copolymer types correspond to compounds of the formulas (I) to (III).

Such copolymers are e.g. polyacrylic acid-co-vinyl-acetate; ethylene/acrylic acid/vinyl acetate copolymers; ethylene/vinyl chloride/acrylic acid/vinyl acetate graft copolymers; acrylic acid/ vinyl acetate/ vinyl chloride copolymers; acrylic acid/vinyl methylether copolymers; vinyl acetate/ acrylic acid/ acrylic acid methylester copolymer; vinyl acetate/ crotonic acid copolymers; vinyl acetate/ maleic acid copolymers; methacrylic acid/ vinyl acetate/ vinyl pyrrolidone copolymers; acrylic acid/ acrylonitrile copolymer; ethylene/ propylene / acrylic acid copolymer; styrene/ acrylic acid copolymer, wherein always a part or all of the acid groups are present in their carboxylate form.

The amount of carboxyl and carboxylate containing moieties within a copolymer will depend on the type

of copolymer. Said amount will generally be from 5 mol % to 50 mol %, preferably from 8 mol % to 40 mol %, and most preferably from 10 mol % to 30 mol %.

The degree of neutralization of the carboxyl groups to form carboxylate groups is preferably from 30 % to 100 % and more preferably from 40 % to 90 %.

5 As mentioned above, the polymer composition comprising the components a) and b) optionally contains one or more essentially water-insoluble hydrophobic polymers (component c), as well as further additives.

The component c) is an essentially water-insoluble polymer or a mixture of such essentially water-insoluble polymers. Component c) is preferably present in an amount effective to enhance the physical properties of articles made from the composition of the invention (which amount is sometimes referred to
10 herein as an "effective amount" of component c)).

As used herein an "essentially water-insoluble thermoplastic polymer" is a polymer which preferably absorbs water at a rate of less than 10 %, preferably less than 5 % per 100 grams of the polymer at room temperature and preferably at a rate of less than 2 % per 100 grams of the polymer at room temperature.

Examples of essentially water-insoluble thermoplastic materials are polyolefines, such as polyethylene
15 (PE), polyisobutylenes, polypropylenes; vinyl polymers such as poly(vinyl chloride) (PVC), poly(vinyl acetates); polystyrenes; polyacrylonitriles (PAN); polyacrylates, polymethacrylates; polyacetals; thermoplastic polycondensates such as polyamides (PA), polyesters, polyurethanes, polycarbonates, poly(alkylene terephthalates); polyarylethers and polyimides; and high molar-mass, essentially water-insoluble or crystallizable poly(alkylene oxides) such as polymers and copolymers of ethylene oxide and propylene oxide.

20 Further included are essentially water-insoluble thermoplastic copolymers known such as alkylene:vinyl ester-copolymers preferably ethylene:vinyl acetate-copolymers (EVA); ethylene:vinyl alcohol-copolymers (EVAL); alkylene:acrylates or methacrylate copolymers preferably ethylene:acrylic acid-copolymers (EAA); ethylene:ethyl acrylate-copolymers (EEA); ethylene:methyl acrylate-copolymers (EMA); ABS-copolymers; styrene:acrylonitrile-copolymers (SAN); styrene-butadiene-copolymers, alkylene:maleic anhydride
25 copolymer preferably ethylene: maleic anhydride copolymer; acrylamide:acrylonitrile copolymers; and mixtures thereof.

Preferred from these are those which undergo melt formation at a set processing temperature preferably within the range of 95 °C to 260 °C, preferably within the range of 140 °C to 210 °C.

Preferred from these are further those polymers containing polar groups such as ether, ester, amide, or
30 urethane groups. Such polymers include e.g. copolymers of ethylene, propylene or isobutylene with vinyl compounds or acrylates such as ethylene:vinyl acetate-copolymers (EVA), ethylene:vinyl alcohol-copolymers (EVAL), ethylene:acrylic acid-copolymers (EAA), ethylene:ethyl acrylate-copolymers (EEA), ethylene:methacrylate-copolymers (EMA), styrene:acrylonitrile-copolymers (SAN); block copolymers of amide-ethers, amide-esters; block copolymers of urethane-ethers, urethane-esters; as well as their mixtures.

35 Most preferred are those polymers containing one type of functional group which is the same type of functional group as that of component b) which is not carboxyl.

Such essentially water-insoluble thermoplastic polymers may be added in any desired amount as described herein.

Such polymers may be used in any known form. Their molecular weight is also generally known in the
40 art. It is also possible to use such polymers of relatively low molecular weight (oligomers). Which molecular weight to choose is a matter of optimization and known to the one skilled in the art.

In the composition according to this invention, the two components a) and b) or the three components a), b) and c) always add up to 100 % and the values of the components (in %) given hereinbelow refer to this sum of 100 %.

45 The ratio of destructurized starch to the component b) and optionally to the sum of the components b) and c) can be 1:99 to 99:1. It is however preferred that the destructurized starch contributes noticeably to the properties of the final material. Therefore, it is preferred that the destructurized starch is present in an amount of at least 20%, more preferably 50% and most preferably in the range of 70% to 99% by weight of the entire composition. That is, component b) is and optionally the sum of the components b) and c) are
50 present in amounts of about 80% or less, more preferably less than or equal to 50% and most preferably in the range of 30% to 1% by weight of the entire composition.

Component b) is a relatively polar material. When it functions in the present compositions in combination with component c), it is able to mix more readily with a more polar component c) than with a less polar one. Accordingly, with more polar components c), relatively less of component b) will be required than with
55 less polar ones. The skilled worker will be able to select appropriate ratios of components b) and c) to obtain a substantially homogenous melt composition.

A mixture of 1 to 15% by weight of the components b) or optionally of the sum of the components b) and c) and 99 to 85% of the destructurized starch shows already a significant improvement in the

properties of the obtained materials. For certain applications a ratio of said components b) or optionally of the sum of the components b) and c) to the destructurized starch component of 1-10% to 99-90% by weight is preferred. If the destructurized starch contains water, the percentage of this destructurized starch component is meant to be the destructurized starch/water component, i.e. including the weight of water.

5 The starch may be mixed with the additives as named hereinbelow to yield a free flowing powder useful for continuous processing and is destructurized and granulated before it is mixed with the components b) and optionally c) or the other optionally added components. The other components to be added are preferably granulated to an equal granular size as the granulated destructurized starch.

10 However, it is possible to process native starch or pre-extruded and/or destructurized granulated or powdered starch together with powdered or granulated additives and/or the polymeric material in any desired mixture or sequence.

Thus, it is preferred that the components a), b) and c) and the additives be mixed in a conventional mixer. This mixture can then be passed through an extruder to produce granulates or pellets as one form of shaped articles useful for further processing. However, it is possible to avoid granulating and to process the obtained melt directly using down-stream equipment to produce films, blown films included, sheets, profiles, pipes, tubes, foams or other shaped articles. The sheets can be used for thermoforming.

It is preferred that the fillers, lubricants and/or plasticizers are added to the starch before destructurization while the addition of the coloring agents as well as of the components b), c) and the other additives can be added before, during or after destructurization.

20 The essentially destructurized starch/water component or granules have a preferred water content in the range of about 10 to 22 % by weight of the starch/water component, preferably 12 to 19% and especially 14 to 18% by weight of the starch/water component.

The water content described above refers to the percentage of water relative to the weight of the starch/water component within the total composition and not to the weight of the total composition itself, which would include also the weight of any added essentially water-insoluble thermoplastic polymer.

25 In order to destructurize the starch and/or to form a melt of the new polymeric composition according to this invention, it is suitably heated in a screw and barrel of an extruder for a time long enough to effect destructurization and melt formation. The temperature is preferably within the range of 105°C to 240°C, more preferably within the range of 130°C to 190°C depending on the type of starch used. For this destructurizing and melt formation, the composition is heated preferably in a closed volume. A closed volume can be a closed vessel or the volume created by the sealing action of the unmolten feed material as happens in the screw and barrel of injection molding or extrusion equipment. In this sense the screw and barrel of an injection molding machine or an extruder is to be understood as being a closed vessel. Pressures created in a closed vessel correspond to the vapour pressure of water at the used temperature but of course additional pressure may be applied and/or generated as normally occurs in a screw and barrel. The preferred applied and/or generated pressures are in the range of pressures which occur in extrusion and are known per se, e.g. from 5 to 150 x 10⁵ N/m² preferably from 5 to 75 x 10⁵ N/m² and most particularly from 5 to 50 x 10⁵ N/m². If the thus-obtained composition is just destructurized starch, it may be granulated and ready to be mixed with the further components according to a chosen mixing and processing procedure to obtain the granular mixture of the destructurized starch/polymer starting material to be fed to the screw barrel.

However, the obtained melt in the screw and barrel may be e.g. injection molded directly into a suitable mold, i.e. directly further processed to a final product if all necessary components are already present.

35 Within the screw, the granular mixture obtained as described above is heated to a temperature which is generally within the range of about 80°C to 240°C, preferably within the range of about 120°C to 220°C and especially within the range of about 130°C to 190°C. Preferably, such mixture is heated to a sufficiently high temperature and for a time long enough until the endothermic transition analysis (DSC) indicates that the specific relatively narrow peak just prior to the endotherm characteristic of oxidative and thermal degradation of starch has disappeared.

50 The minimum pressures under which the melts are formed correspond to the water vapour pressures produced at said temperatures. The process is carried out in a closed volume as explained above, i.e. in the range of the pressures which occur in extrusion or molding processes and known per se, e.g. from zero to 150 x 10⁵ N/m² preferably from zero to 75 x 10⁵ N/m² and most particularly from zero to 50 x 10⁵ N/m².

When forming a shaped article by extrusion the pressures are preferably as mentioned above. If the melt according to this invention is, e.g., injection molded, the normal range of injection pressures used in injection molding is applied, e.g. from 300 x 10⁵ N/m² to 3000 x 10⁵ N/m² and preferably from 700 x 10⁵ to 2200 x 10⁵ N/m².

Accordingly, the present invention provides a thermoplastic destructurized-starch substantially homo-

genous melt formed by the process comprising:

1) providing a mixture comprising starch and at least one polymer which does not contain hydroxyl groups and is selected from the group consisting of polymers which contain at least two types of functional groups bound to the same molecule one type of these groups being carboxylate groups (component b); and

2) heating said mixture in a closed volume under sufficient temperature and pressure for a time long enough to effect destructurization of said starch and form said melt.

The present invention also provides a thermoplastic destructurized-starch product having substantial dimensional stability formed by the process comprising:

1) providing a mixture comprising starch and at least one polymer which does not contain hydroxyl groups and is selected from the group consisting of polymers which contain at least two types of functional groups bound to the same molecule one type of these groups being carboxylate groups (component b);

2) heating said mixture in a closed volume under sufficient temperature and pressure for a time long enough to effect destructurization of said starch and form a substantially homogenous melt;

3) shaping said melt into an article; and

4) allowing said shaped article to cool to a substantially dimensionally stable thermoplastic product.

The mixture provided in step 1) of either above-described processes may additionally contain component c) and additives as described herein.

Various hydrophilic polymers may be used as additives. These include water-soluble and water-swellaable polymers. As such it includes animal gelatin, vegetable gelatins resp. proteins such as sunflower protein, soybean proteins, cotton seed proteins, peanut proteins, rape seed proteins, acrylated proteins; water-soluble polysaccharides, alkyl celluloses, hydroxyalkyl celluloses and hydroxyalkylalkyl celluloses, such as:

methyl cellulose, hydroxymethyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, hydroxyethylmethyl cellulose, hydroxypropylmethyl cellulose, hydroxybutylmethyl cellulose, cellulose esters and hydroxyalkyl cellulose esters such as:

cellulose acetylphthalate (CAP), Hydroxypropylmethylcellulose (HPMCP); carboxyalkyl celluloses, carboxyalkyl-alkyl celluloses, carboxyalkyl cellulose, analogous known polymers made from starch; carboxymethyl cellulose and their alkalimetal salts; water-soluble or water-swellaable synthetic polymers such as: polyvinyl alcohols, polyvinyl acetatephthalates (PVAP), polyvinyl pyrrolidone, suitable are also phthalated gelatin, gelatin succinate, crosslinked gelatin, shellac, cationically modified acrylates and methacrylates possessing, for example, a tertiary or quaternary amino group, such as the diethylaminoethyl group, which may be quaternized if desired; and other similar polymers.

Such hydrophilic polymers may optionally be added up to 50 % based on the starch/water component, preferably up to 30 % and most preferably between 5% and 20% based on the starch/water component. If any hydrophilic polymer is added, its mass should be considered along with the starch in determining the appropriate amount of water in the composition.

Other useful additives may be e.g. adjuvants, fillers, lubricants, mold release agents, plasticizers, foaming agents, stabilizers, coloring agents, pigments, extenders, chemical modifiers, flow accelerators, and mixtures thereof.

Examples for fillers are inorganic fillers, such as the oxides of magnesium, aluminum, silicon, titanium, etc. preferably in a concentration in the range of about 0.02 to 50 % by weight preferably 0.20 to 20 % based on the total weight of all the components.

Examples for lubricants are stearates of aluminum, calcium, magnesium and tin as well as talc, silicones, etc. which may be present in concentrations of about 0.1 - 5% preferably at 0.1 - 3% based upon the weight of the total composition.

Examples of plasticizers include low molecular poly(alkylene oxides), such as poly(ethylene glycols), poly(propylene glycols), poly(ethylene-propylene glycols); organic plasticizers of low molar masses, such as glycerol, pentaerythritol, glycerol monoacetate, diacetate or triacetate; propylene glycol, sorbitol, sodium diethylsulfosuccinate, etc., added in concentrations ranging from 0.5 to 15%, preferably ranging from 0.5 to 5% based on the total weight of all the components. Examples of colouring agents include known azo dyes, organic or inorganic pigments, or colouring agents of natural origin. Inorganic pigments are preferred, such as the oxides of iron or titanium, these oxides, known per se, being added in concentrations ranging from 0.001 to 10%, preferably 0.5 to 3%, based on the weight of all the components.

There may further be added compounds to improve the flow properties of the starch material such as animal or vegetable fats, preferably in their hydrogenated form, especially those which are solid at room temperature. These fats have preferably a melting point of 50 °C or higher. Preferred are triglycerides of C₁₂ -, C₁₄ -, C₁₅ -, and C₁₈ - fatty acids.

These fats can be added alone without adding extenders or plasticizers.

These fats can advantageously be added alone or together with mono- and/or diglycerides or phosphatides, especially lecithin. The mono- and diglycerides are preferably derived from the types of fats described above, i.e. from C_{12} -, C_{14} -, C_{16} -, and C_{18} - fatty acids.

The total amount of fats, mono-, diglycerides and/or lecithins used are up to 5% and preferably within the range of about 0.5 to 2% by weight of the total weight of starch and any added hydrophilic polymer.

The materials may further contain stabilizers, such as antioxydants, e.g. thiobisphenols, alkyliden-bisphenols secondary aromatic amines; light stabilizers such as UV-absorbers and UV-quenchers; hydroperoxide decomposer; free-radical scavengers; stabilizers against microorganisms.

The compositions of the invention form thermoplastic melts on heating and in a closed volume, i.e. under conditions of controlled water-content and pressure. Such melts can be processed just like conventional thermoplastic materials, using, for example, conventional apparatus for injection molding, blow molding, extrusion and coextrusion (rod, pipe and film extrusion), compression molding, foaming, to produce known articles. The articles include bottles, sheets, films, packaging materials, pipes, rods, laminated films, sacks, bags, pharmaceutical capsules, granules, powders or foams.

For example, these compositions may be used to prepare low density packaging materials (e.g. foams) by well-known methods. Conventional blowing agents may be utilized if desired or, for certain compositions, the water itself may act as the blowing agent. Open cell and closed cell foams may be produced as desired by varying the composition and processing conditions. These foams produced from the present compositions will demonstrate improved properties (e.g., dimensional stability, moisture resistance, etc.) when compared with foams made of starch without incorporation of the components b) and c) according to this invention.

These compositions may be used as carrier materials for active substances, and may be mixed with active ingredients such as pharmaceuticals and/or agriculturally active compounds such as insecticides or pesticides for subsequent release applications of these ingredients. The resulting extruded materials can be granulated or worked to fine powders.

The following examples are provided to further explain and exemplify the invention but not to limit the scope thereof, which scope is defined by the appended claims.

30 Example 1

(a) 5000 g of potato starch containing 14.87 % water are placed in a high speed mixer and 485 g of water are added under stirring. To the above mixture of starch and water, 425 g of crotonic acid-co-vinyl acetate, sodium salt (component b)) containing 13 % of the monomeric units as vinyl acetate and 87 % of the monomeric units as crotonic acid of which 90 % are in form of sodium salt and 42 g of polyethylene-co-vinyl acetate (component c)) containing 80 % of the monomeric units as ethylene and 20 % of the monomeric units as vinyl acetate (sold as Escorene UL02020 by Exxon); 42.5 g of hydrogenated fat (lubricant/release agent) sold as Boeson VP by Boehringer Ingelheim; 21.25 g of a melt flow accelerator (lecithin) and 21.25 g of titanium dioxide (pigment and solid mixture flow accelerator) are added under stirring. The water content of the final mixture is 20 %.

(b) 5000 g of the mixture prepared under (a) are fed through a hopper into a Leistritz Single Screen Lab Extruder LSM 30 having a temperature profile of 55 °C/ 145 °C/ 165 °C/ 165 °C with an output of extrudate of 100 g/min.

The extrudate is cut into granulates and the water content is determined to be 13.10 %. The granulates are then brought back to a water content of 17 % by spraying of water under stirring in a conventional mixer.

(c) The granulates of the pre-blended mixture as obtained under (b) are fed through a hopper to an injection-molding machine Kloeckner-Ferromatic FM 60, for the production of tensile test pieces. The processing conditions are the following: temperature profile: 90 °C/ 155 °C/ 155 °C/ 155 °C, shot weight: 8.2 g, residence time: 450 sec., injection pressure: 1800 bar, back pressure: 30 bar.

All the tensile test pieces are conditioned in a climatic cabinet at 50 % R.H. for five days as an arbitrary standard condition.

The test pieces are of standard DIN design (DIN No. 53455).

(d) The conditioned tensile test pieces are then tested for their stress/strain behaviour on an Instron tensile test apparatus, each test with 4 pieces.

The samples are measured at room temperature using an extension rate of 10 mm per minute. Results are presented in Table 1 and compared with those obtained with tensile test pieces obtained from the same starch processed in a similar way but in absence of components b) and c).

The break strain (elongation at break) going from 15.82 % to 31.20 % and break energy from 194.30 kJ/m² to 395.25 kJ/m² showing a considerable increase in the toughness of the blend material over the unblended one.

Of course blend compositions show different values for the physical parameters indicated. To obtain the best values is a matter of optimization by varying the concentration of the different components, which is no problem to the expert in the art.

Table 1

	Break Strain	Break Energy
	(%)	(kJ/m ²)
starch (unblended starch)	15.82	194.3
ternary blend Example 1	31.20	395.25

Example 1 is repeated with the following blends as per the Examples 2 to 6 whereby analogous results as given in Table 1 are obtained.

Example 2

Example 1 is repeated except that the ratio of the components is varied as given in Table 2. For comparison perspective, Example 1 is shown as Blend No. 1.

Table 2

Blend No.	starch: component b) + c) (weight ratio)	component b): component c) (weight ratio)
2	50 : 50	100 : 0
3	60 : 40	99 : 1
4	70 : 30	50 : 1
5	80 : 20	20 : 1
Ex.1	91.5 : 8.5	10 : 1
6	90 : 10	1 : 1
7	94 : 6	1 : 10
8	98 : 2	1 : 50
9	99 : 1	1 : 99

The resulting injection molded polymers are tougher and more resistant to humid air than the unmodified starch polymer. The toughness as judged by resistance to breaking upon bending increases from blend 9 to blend 2 in concert with the combined increase in crotonic acid-co-vinyl acetate, sodium salt content. While the resistance to softening in humid atmosphere is improved in all cases relative to unmodified starch, the resistance of blends 1,4,5 and 6 are particularly good. These results illustrate the unexpected combinations as benefits in performance.

Example 3

Example 1 is repeated by using 800 g of the same polyvinylcrotonic acid-co-vinyl acetate, sodium salt (component b) instead of 425 g and 250 g of the same polyethylene-co-vinyl acetate (component c) instead of 42 g.

The resulting injection molded polymer is tougher and more resistant to humid air than unblended starch polymer.

5 Example 4

Example 1 is repeated by using 1200 g of the same polyvinylcrotonic acid-co-vinyl acetate, sodium salt (component b) instead of 425 g and 500 g of the same polyethylene-co-vinyl acetate Escorene UL02020 (component c) instead of 42 g.

10 The resulting injection molded polymer is tougher and more resistant to humid air than unblended starch polymer.

15 Example 5

Example 1 is repeated but without polyethylene-co-vinyl acetate (component c).
The results obtained are shown in Table 3.

Table 3

	Break Strain	Break Energy
	(%)	(kJ/m ²)
starch (unblended starch)	16.00	195.00
binary blend Example 1	26.00	350.00

20
25
30 These results show an increase of break strain and break energy (increase of strength and toughness of the binary blend).

In a further run the content of the polyvinylcrotonic acid-co-vinyl acetate, sodium salt of the binary blend is increased to 850 g and 2125 g respectively.

35 The physical-mechanical properties of the resulting injection molded polymers are superior to those of the unblended starch.

Example 6

40 Example 5 with binary blend is repeated but by replacing the 425 g of polycrotonic acid-co-vinyl acetate, sodium salt (component b) by 850 g of polymethylmethacrylate-co-methacrylic acid, sodium salt having the following composition: 80 % of the monomeric units as methylmethacrylate and 20 % of the monomeric units as methacrylic acid of which 90 % are in form of sodium salt. The results are shown in Table 4.

45 The obtained injection molded test pieces show improved physical-mechanical properties as compared to those of unblended starch.

50

55

Table 4

	Break Strain	Break Energy
	(%)	(kJ/m ²)
starch (unblended starch)	16.00	195.00
binary blend Example 6	35.00	400.00
binary blend Example 7	45.00	700.00

Example 7

Example 6 is repeated but in using 1700 g of polymethyl methacrylate-co-methacrylic acid, sodium salt (component b) instead of 850 g. The physical-mechanical properties of the obtained test pieces are shown on Table 4. It can be seen that these properties compared to those of unblended starch are considerably better.

Example 8

(a) 5000 g of potato starch containing 15.1 % water are placed in a high speed mixer and 130 g of polymethylmethacrylate-co-methacrylic acid, sodium salt component b) described in Example 6; 85 g of Nylon 12 sold by Huels Chemie as Vestamid L-1700; 42.5 g of hydrogenated fat (lubricant release agent) sold as Boeson VP by Boehringer Ingelheim, 21.25 g of a melt flow accelerator (lecithin) sold as Metarin P by Lucas Meyer are added under stirring. The water content of the final mixture is 14.2 %.

(b) 5000g of the mixture prepared under (a) are fed through a hopper into a Werner & Pfleiderer co-rotating twin screw extruder (model Continua 37).

The temperature profile of the four sections of the barrel is respectively 20 °C; 80 °C; 220 °C; 100 °C.

Extrusion is carried out with a mixture output of 8 kg/hr (screw speed 200 rpm). Water is added at the inlet with a flow rate of 4.1 kgs/hr. The water content of the material during extrusion is therefore 31.5 %. In the last section of the extruder 300 mbar reduced pressure is applied to remove part of the water as water vapour.

The water content of the granulates is 17.4 % as measured after they have equilibrated at room temperature.

(c) The granulates of the pre-blended mixture as obtained under (b) (H₂O content: 17.4 %) are fed through a hopper to an injection molding machine Arburg 329-210-750 for the production of tensile test pieces. The temperature profile of the barrel is: 90 °C/ 155 °C/ 155 °C/ 155 °C.

The shot weight is 8 g, the residence time 450 sec., the injection pressure 1833 bar, the back pressure 80 bar, the screw speed 180 rpm.

All the tensile test pieces were conditioned in a climatic cabinet at 50 % R.H. for five days as an arbitrary standard condition.

The test pieces are of standard DIN design (DIN No. 53455).

(d) The conditioned tensile test pieces are then tested for their stress/strain behaviour on a Zwick tensile test apparatus.

The samples are measured at room temperature using an extension rate of 10 mm per minute. The physical-mechanical properties of the corresponding injection molded test pieces are superior to those of the unblended starch.

Example 9

(a) 2100 g of potato starch containing 15 % water are placed in a high speed mixer and 765 g of acrylamide-co-acrylic acid, sodium salt (component b) (containing 90 mole % acrylamide and 10 mole %

acrylic acid, sodium salt. 5950 g of thermoplastic polyamide elastomer (component c)) sold as Pebax MA-4011 by Atochem; 17.85 g of hydrogenated fat (lubricant/release agent) Boeson VP and 8.93 g of a melt flow accelerator (lecithin/Metarin P) are added under stirring. The water content of the final mixture is 13.5 %.

- 5 (b) 8000 g of the mixture prepared under (a) are fed through a hopper into the same twin-screw co-rotating extruder described in Example 8. The extrusion of the mixture is carried out with the same temperature profile: 20 °C/ 80 °C/ 240 °C/ 80 °C. The other parameters of the extrusion experiment are the following:

material output: 9 kg/hr

- 10 screw speed: 200 rpm

water added: 1.8 kg/hr

reduced pressure (last section) 500 mbar

water-content during extrusion: 28.6 %

- 15 The water content of the granulates is 6.95 % as measured after they had equilibrated at room temperature. The granulates are then remoistened to 17 % H₂O.

(c) The granulates obtained under (b) are processed using the same injection molding machine described in (c) of Example 8. The temperature profile of the barrel is 90 °C/ 155 °C/ 155 °C/ 155 °C. The other processing parameters were:

- 20 shot weight: 6.6 g

residence time: 450 sec.

injection pressure: 550 bar

back pressure: 80 bar

screw speed: 180 rpm

- 25 The tensile test pieces thus produced are conditioned and tested on a Zwick tensile test apparatus as described in (d) of Example 8.

Results are presented in Table 5.

Table 5

	Break Strain	Break Energy
	(%)	(kJ.m ²)
35 starch (unblended starch)	22.00	325.00
ternary blend Example 9	200.00	850.00

Example 10

- 45 Example 8 is repeated replacing the 130 g of the polymethylmethacrylate-co-methacrylic acid, sodium salt (component b) by 425 g of polycrotonic acid-co-vinyl acetate, sodium salt and the 85 g of Nylon 12 Vestamid L-1700 by 85 g of a thermoplastic polyamide elastomer sold as PEBAX MA-4011 by Atochem (component c).

- 50 The physical-mechanical properties of the corresponding injection molded test pieces are superior to those of the unblended starch.

Example 11

- 55 Example 10 is repeated using 210 g of polycrotonic acid-co-vinyl acetate, sodium salt (component b) instead of 425 g. To this polymer 425 g of thermoplastic polyamide elastomer sold as PEBAX MA-4011 (component c) by Atochem and 425 g of thermoplastic polyurethane elastomer sold as Pellethane 2103-80-AE (component c) sold by Dow Chemical Co. are added in Section a).

The physical-mechanical properties of the corresponding injection molded test pieces are superior to

those of the unblended starch.

Example 12

Example 11 is repeated in adding to the other components 42.5 g of polyethylene sold as Lupolen 2410 T by BASF (third component c).

The physical-mechanical properties of the corresponding injection molded test pieces are superior to those of the unblended starch.

Example 13

Example 8 (Section a) is repeated.

b) 5000 g of the mixture prepared under Section a) are fed through a hopper into a Werner-Pfleiderer co-rotating twin screw extruder (model Continua 37) and processing carried out in a similar way as the one described in Section b) of Example 8. Water added at the inlet is adjusted so that the water content of the material is 21 % by weight. The cutter is removed from the die face and a continuous extrudate is obtained which is foamed as a result of the excess water evaporation. The foam is chopped into 30-40 mm lengths and is useful as a loose-fill, packaging insulation material.

Example 14

During each of the injection molding operations in Examples 1 - 12 an experiment is performed to demonstrate the utility of making foams. The molten material which is obtained as described in Example 1, in Example 8, Sections a), b) and c) in each case is extruded into the open atmosphere (Section c) instead of being injection molded into a closed mold. In every case the material is converted into a foamed extrudate useful for loose-fill in packaging applications.

Example 15

The granulates from Example 1 are mixed with polystyrene in the proportion of 30 to 70 parts by weight and are treated according to Example 13 (Section b) The resulting foamed extrudate contains a very fine and uniform cell structure suitable for a variety of uses including structural foam.

Claims

1. A composition of matter capable of being formed into articles having substantial dimensional stability comprising

a) a destructureized starch, and

b) at least one polymer which does not contain hydroxyl groups and is selected from the group consisting of polymers which contain at least two types of functional groups bound to the same molecule one type of these groups being carboxylate groups said polymer being present in an amount effective to enhance the physical properties of said articles.

2. A composition according to claim 1 wherein the polymer of component b) further contains alkoxy, carboxyalkyl, alkyl carboxy, halo and/or pyrrolidono groups.

3. A composition according to claim 1 wherein the component b) is a synthetic polymer as obtained by copolymerization of acrylic acid, methacrylic acid, crotonic acid, maleic acid, itaconic acid, with monomers selected from the group consisting of ethylene, vinyl chloride, vinyl esters, acrylic acid esters, acrylonitrile, methacrylic acid esters, maleic acid esters, acryl amide, vinylene carbonate, omega-octadecene, vinyl-butyl ether, vinyl pyrrolidone.

4. A composition according to claim 1 wherein the component b) is derived from acrylic acid, methacrylic acid, crotonic acid, maleic acid, itaconic acid, methylacrylate, methylmethacrylate, acrylamide, acrylonitrile and/or methylvinyl ether.

5. A composition according to anyone of the claims 1 to 5 wherein the amount of carboxyl and

carboxylate containing moieties within the copolymer is from 5 mol % to 50 mol %.

6. A composition according to anyone of the claims 1 to 5 wherein the degree of neutralization of the carboxyl groups to form carboxylate groups is from about 30 % to about 100 %.

7. A composition according to claim 1 wherein component b) is selected from the group consisting of polyacrylic acid-co-vinyl- acetate; ethylene/acrylic acid/vinyl acetate copolymers; ethylene/vinyl chloride/acrylic acid/vinyl acetate graft copolymers; acrylic acid/ vinyl acetate/ vinyl chloride copolymers; acrylic acid/vinyl methylether copolymers; vinyl acetate/ acrylic acid/ acrylic acid methylester copolymer; vinyl acetate/ crotonic acid copolymers; vinyl acetate/ maleic acid copolymers; methacrylic acid/ vinyl acetate/ vinyl pyrrolidone copolymers; ethylene/ acrylic acid/methylacrylate copolymer; acrylic acid/acrylonitrile copolymer; ethylene/ propylene /acrylic acid copolymer; styrene/ acrylic acid copolymer.

8. The composition according to anyone of the claims 1 to 7 wherein the weight % ratio of destructurized starch to component b) is about 1:99 to about 99:1.

9. The composition according to claim 8 wherein destructurized starch is present in amounts of about 50 % to about 99 % by weight of the total composition.

10. The composition according to anyone of the claims 1 to 9 wherein the destructurized starch has a water content of about 5 % to about 40 %, and preferably of about 10 % to about 22 % by weight of the total starch content.

11. The composition according to anyone of the claims 1 to 10 wherein there is additionally incorporated component c) comprising an substantially water-insoluble thermoplastic polymer which does not fall within the definition of those compounds defined as component b).

12. The composition according to claim 11 wherein said component c) is selected from the group consisting of polyolefines, vinyl polymers, polystyrenes, polyacrylonitriles, poly(vinyl carbazols), polyacrylates, polymethacrylates, polyacetals, thermoplastic polycondensates, polyarylethers, thermoplastic polyimides, polyhydroxybutyrate, high molar-mass substantially water-insoluble or crystallizable poly-(alkylene oxides).

13. The composition of claim 12 wherein component c) is selected from the group consisting of polyethylenes, polypropylenes, polyisobutylenes, poly(vinyl chlorides), poly(vinyl acetate), polystyrene, polyamides, thermoplastic polyesters, thermoplastic polyurethanes, polycarbonates, poly(alkylene terephthalates) and mixtures thereof.

14. The composition according to claims 11 wherein component c) is selected from the group consisting of thermoplastic alkylene/vinyl ester-copolymers; ethylene/vinyl alcohol-copolymers; alkylene/acrylates or methacrylate copolymers; ABS-copolymers; styrene/acrylonitrile-copolymers; styrene-butadiene-copolymers, alkylene/maleic anhydride copolymer; partially hydrolyzed polyacrylates or polymethacrylates; partially hydrolyzed copolymers of acrylates and methacrylates; acrylic acid esters/acrylonitrile copolymers and hydrolysates thereof; acrylamide/acrylonitrile copolymers; and mixtures thereof.

15. A composition according to claim 14 wherein component c) is selected from the group consisting of ethylene/vinyl acetate-copolymers, ethylene/vinyl alcohol-copolymers, ethylene/acrylic acid-copolymers, ethylene/ethyl acrylate-copolymers, ethylene/methacrylate-copolymers, styrene/acrylonitrile-copolymers; block copolymers of urethane-ethers, urethane-esters; as well as their mixtures.

16. The composition according to anyone of the claims 11 to 15 wherein the sum of components b) and c) constitute about 1 % to about 99 %, preferably about 20 % to about 80 % and most preferably about 1 % to about 30 % by weight of the total composition.

17. The composition according to anyone of the claims 1 to 16 wherein there are additionally incorporated one or more materials selected from the group consisting of adjuvants, fillers, lubricants, mold release agents, plasticizers, foaming agents, stabilizers, extenders, chemical modifiers, flow accelerators, coloring agents, pigments and mixtures thereof.

18. The composition according to claim 17 further containing an agriculturally active compound.

19. The composition according to anyone of the claims 1 to 18 which is a melt blend.

20. The composition according to claim 19 which is a cooled solidified blend.

21. The composition according to claim 20 in particulate, granulated or pelletized form.

22. A thermoplastic destructurized-starch product made from a composition as claimed in anyone of the claims 1 to 18, 20 and 21 having substantial dimensional stability formed by the process comprising:

1) providing a mixture comprising starch and at least one polymer which does not contain hydroxyl groups and is selected from the group consisting of polymers which contain at least two types of functional groups bount to the same molecule one type of these groups being carboxylate groups (component b); and

2) heating said mixture in a closed volume under sufficient temperature and pressure for a time long enough to effect destructurization of said starch and form a substantially homogenous melt;

3) shaping said melt into an article; and

4) allowing said shaped article to cool to a substantially dimensionally stable thermoplastic product.

23. The product according to claim 22 wherein destructurization of the starch is carried out at a temperature above its melting point and glass transition temperature.

24. The product according to claim 23 wherein the destructurization of the starch is carried out at temperatures of about 105 °C to about 240 °C, preferably at a temperature of about 130 °C to about 190 °C.

25. The product according to claim 23 wherein the melt is formed under the range of pressure from the minimum pressure necessary to avoid formation of water vapour under the applied temperature up to about $150 \times 10^5 \text{ N/m}^2$

26. The product according to claim 25 wherein the heat and pressure are maintained until the starch has undergone the specific narrow endothermic transition just prior to its endothermic change characteristic of oxidative and thermal degradation.

27. The product according to anyone of the claims 22 to 26 which is a granulate, a pellet or a powder.

28. The product according to claim 27 further melted and processed to form a shaped article selected from the group consisting of containers, bottles, pipes, rods, packaging material, sheets, foams, films, sacks, bags and pharmaceutical capsules.

29. The shaped articles according to claim 28 wherein the further melting and processing comprises foaming, filming, compression molding, injection molding, blow molding, extruding, co-extruding, vacuum forming, thermoforming and combinations thereof.

30. A thermoplastic destructurized-starch substantially homogenous melt made from a composition as claimed in anyone of the claims 1 to 18, 20 and 21 formed by the process comprising:

1) providing a mixture comprising starch and at least one polymer which does not contain hydroxyl groups and is selected from the group consisting of polymers which contain at least two types of functional groups bount to the same molecule one type of these groups being carboxylate groups (component b); and

2) heating said mixture in a closed volume under sufficient temperature and pressure for a time long enough to effect destructurization of said starch and form a substantially homogenous melt:

3) shaping said melt into an article; and

4) allowing said shaped article to cool to a substantially dimensionally stable thermoplastic product.

31. The melt according to claim 30 wherein destructurization of the starch is carried out at a temperature above its melting point and glass transition temperature.

32. The melt according to claim 31 wherein destructurization of the starch is carried out at a temperature of about 105 °C to about 240 °C, preferably at a temperature of about 130 °C to about 190 °C.

33. The melt according to claim 32 wherein the melt is formed under the range of pressure from the minimum pressure necessary to avoid formation of water vapour under the applied temperature up to about $150 \times 10^5 \text{ N/m}^2$

34. The melt according to claim 33 wherein the heat and pressure are maintained until the starch has undergone the specific narrow endothermic transition just prior to its endothermic change characteristic of oxidative and thermal degradation.

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) Publication number:

0 404 727 A3

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: 90810440.9

(51) Int. Cl.⁵: **C08L 3/02, C08L 57/10,
C08L 33/00**

(22) Date of filing: 18.06.90

(30) Priority: 22.06.89 US 369978
02.11.89 US 430764(43) Date of publication of application:
27.12.90 Bulletin 90/52(94) Designated Contracting States:
AT BE CH DE DK ES FR GB GR IT LI LU NL SE(88) Date of deferred publication of the search report:
22.05.91 Bulletin 91/21(71) Applicant: **WARNER-LAMBERT COMPANY**
201 Tabor Road
Morris Plains New Jersey 07950(US)(72) Inventor: **Lentz, David John, Dr.**
23 Timber Lane
Randolph, N.J. 07869(US)
Inventor: **Sachetto, Jean-Pierre, Dr.**
Düchelweiher 13
CH-4144 Arlesheim(CH)
Inventor: **Silbiger, Jakob, Dr.**
Oberwilerstrasse 72
CH-4054 Basel(CH)(74) Representative: **Silbiger, Jakob, Dr.**
c/o **CAPSUGEL AG** Fabrikmattenweg 2-4
CH-4144 Arlesheim(CH)(54) **Polymer base blend compositions containing destructurized starch.**

- (57) A thermoplastic polymer composition comprising
- a) a destructurized starch, and
 - b) at least one polymer which does not contain hydroxyl groups and is selected from the group consisting of polymers which contain at least two types of functional groups bound to the same molecule one type of these groups being carboxylate groups; said polymer being present in an amount effective to enhance the physical properties of said articles.

The composition may contain further conventional additives as well as hydrophobic, substantially water-insoluble polymers.

EP 0 404 727 A3



European
Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 90 81 0440

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
P,A	EP-A-0 344 118 (WARNER-LAMBERT CO.) - - -		C 08 L 3/02
A	EP-A-0 132 299 (USA SECRETARY US DEPARTMENT OF COMMERCE) - - -		C 08 L 57/10 C 08 L 33/00 // (C 08 L 3/02
Y	GB-A-2 190 093 (WARNER-LAMBERT CO.) * Page 2, lines 56-58; claims *	1-34	C 08 L 33:02 C 08 L 23:08) (C 08 L 3/02
Y	EP-A-0 253 490 (MERCK) * Page 3, lines 25-31 * - - - - -	1-34	C 08 L 33:12 C 08 L 77:02) (C 08 L 3/02 C 08 L 33:26 C 08 L 77:02)
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C 08 L
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of search 04 March 91	Examiner LENSEN H.W.M.
<div>CATEGORY OF CITED DOCUMENTS</div> <div>X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention</div> <div>E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons ----- &: member of the same patent family, corresponding document</div>			